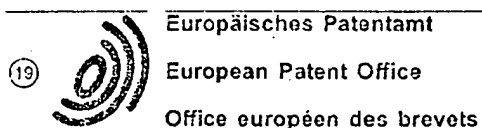


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(54) Antifouling paint.

(57) An antifouling paint containing as active component, suitably in an amount of 5 to 100% by weight of the total non-volatiles, an alkylphenoxy group-containing organo-silicon compound (such as an organo-silane, bis-silyl compound or polysiloxane) in which compound the alkyl substituent is a straight or branched C₇ to C₁₂ alkyl group or a 1-methyl-1-phenylethyl group.

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Field of the invention

The present invention relates to an antifouling paint which is less toxic to human being, is very safe to surrounding and has a strong antifouling effect.

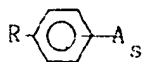
Background of the invention

Marine structures, inclusive of ships, offshore structures, sea water conduit systems of seaside plants, fish-nets, culture rafts and buoys, are favorite habitats of large attached animals and plants, such as barnacle, hard-shell mussel, sea lettuce (green laver), etc., attached diatoma, bacteria and other microorganisms, all of which cause corrosion of structures, increased seawater resistance of slips, clogging of fishnets which may induce a massive death of fish, and increased structure weights which lead to sinking and decreased operation efficiencies.

In order to prevent such damages due to harmful aquatic life, the submerged structures, ships, fishnets and the like have heretofore been coated with antifouling paints which are mostly based on organocopper compounds or organotin compounds. Such paints are usually compounded with, as a part of coating vehicle, rosin and the toxicant is usually dissolved out of the coating with the said rosin.

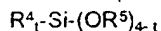
Also, an antifouling paint containing as resinous vehicle a trialkyl tin polymer has been used as an hydrolysis type antifouling paint. In this type of paint, the trialkyl tin polymer is hydrolyzed in a weak alkaline sea water, liberating an organotin compound and at the same time, the polymer vehicle is turned to be of soluble type and gradually dissolved in sea water together with the toxic organotin compound. In either type of antifouling paints, the dissolved toxicants are very toxic to the sea living thereby killing or weakening the animals or plants and attaining the antifouling effects desired. These toxicants are also harmful to human being and hence the heretofore proposed paints have serious problems in safety and hygienic standviews for operators and environmental air pollution.

The inventors have formerly made a proposal in Japanese Patent Application No. 59344/90 (Publication No.128302/91) of a noxious aquatic control agent containing as a toxicant an alkyl substituted phenol derivative of the formula:

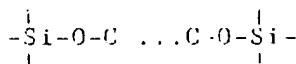


in which R is a straight or branched alkyl having 3 to 21 carbon atoms; A is hydrogen atom, hydroxy group or methoxy group; and s is an integer of 1 to 5, providing that at least one A is hydroxy or methoxy group. However, an antifouling paint containing the abovementioned phenol derivative is not so useful because of the soluble natures of the toxicant.

Furthermore, in Japanese Patent Application No. 224452/62, has been proposed a coating composition containing as a vehicle a reaction product of a silane compound represented by the formula:



in which R⁴ is alkyl group, haloalkyl group, cycloalkyl group, aryl group or aralkyl group, R⁵ is hydrogen atom, alkyl group or cycloalkyl group, and t is 0 or an integer of 1 to 3, and/or its low condensation product, an organic compound having in its molecule at least 2 hydroxyl groups, and monohydric phenol compound. The coating obtained is said to have a strong and long-lasting antifouling and anti-mold effects due to the strong antibacterial and anti-mold activities of the monohydric phenol component attached to silane and the activities of the main structural portion of the formula:

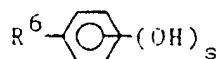


In that patent application, the following are mentioned as examples of the monohydric phenol compound: phenol; alkyl phenols as o-cresol, m-cresol, p-cresol, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 2,6-xyleneol, 3,4-xyleneol, 3,5-xyleneol, o-ethyl phenol, m-ethyl phenol, p-ethyl phenol, p-t-amyl phenol, p-t-butyl phenol, p-phenyl phenol, p-cyclohexyl phenol; alkoxy phenols as m-methoxy phenol; halogen substituted phenols as o-chlorophenol, p-chlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2,4,6-tribromophenol; nitrophenols as o-nitro phenol, p-nitro phenol, 2,4-dinitro phenol, 2,4,6-trinitrophenol; amino substituted phenols as p-dimethylamino phenol; cyano phenols as p-cyanophenol and the like.

However, these phenols are comparatively water soluble and therefore, when hydrolyzed and released in the environment, there are problems in safety. Furthermore, the desired long-lasting antifouling effects cannot be attained because they are, after being hydrolyzed, quickly dissolved out in sea water due to their excellent water solubilities.

Alkoxy, halogen, nitro, amino and cyano substituted phenols are much highly water soluble, causing harmful effects in surroundings.

The inventors have also previously proposed in Japanese Patent Application No. 127025/91 an antifouling composition for fishnet use comprising an alkyl phenol compound of the formula:



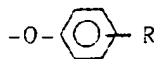
in which R^6 is a straight or branched alkyl having 4 to 21 carbon atoms; and s is an integer of 1 to 5, repellent compound as silicone oil, and antifouling agent as dichlorophenyl dimethyl urea. However, this is likewise still in short in the antifouling activities and further improvement has long been desired.

As another attempts for utilizing phenol compounds in antifouling paints, have been proposed in Japanese Patent Application Nos. 286355/89, 316814/89, 55396/88, 21751/88, and 50232/88, polymers or copolymers of vinyl monomers to which various phenol compounds are connected through ester bond and phenol modified resins derived from the compounds obtained by the addition reaction of various phenols and carboxylic anhydrides. In these polymers, phenol compounds are connected to their side chains through ester bonds and such phenol esters are believed to be quite difficult in the control of their hydrolysis rates in sea water.

It is, therefore, an object of the invention to provide a novel and effective antifouling paint being free from the abovementioned problems.

Summary of the invention

According to the present invention, the abovementioned object can be attained by the antifouling paint consisting essentially of an alkylphenoxy group containing organo-silicon compound having in its molecule at least one alkylphenoxy group of the formula:



in which R stands for a straight or branched chain alkyl group of the formula: C_xH_{2x+1}

in which x is an integer of 7 to 12,

or 1-methyl-1-phenylethyl group, in an amount of 5 to 100% by weight of the non-volatile of the paint, and a solvent.

More specifically, the abovementioned alkyl phenoxy group containing organo-silicon compound is either one of the following:

(1) silane compound containing at least one alkylphenoxy group of the formula:

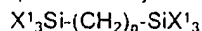


in which R stands for a straight or branched chain alkyl group of the formula: C_xH_{2x+1}

in which x is an integer of 7 to 12,

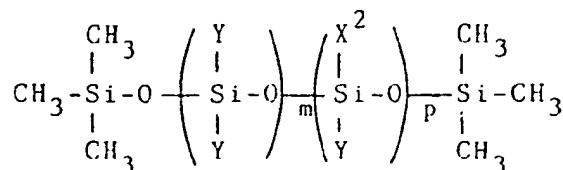
or 1-methyl-1-phenylethyl group

(2) an alkylphenoxy bis-silyl compound represented by the formula:



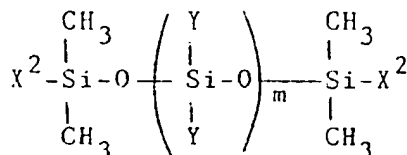
in which X^1 is selected from the group consisting of hydrogen atom, hydroxy group, lower alkyl group having 1 to 5 carbon atoms, lower alkoxy group having 1 to 5 carbon atoms, phenyl group, phenoxy group, vinyl group, acetoxy group, propenyloxy group, methyl ethyl ketoxim group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one of said X^1 is the straight or branched chain alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group, and n is an integer of 1 to 10,

(3) an alkylphenoxy polysiloxane represented by the formula:



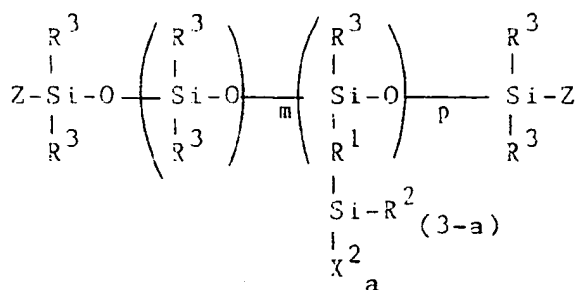
, having a number average molecular weight of less than 100,000 in which Y is the same or different substituents and each represents a member selected from the group consisting of alkyl having 1 to 3 carbon atoms, vinyl group and phenyl group; X² is a member selected from the group consisting of hydrogen atom, halogen atom, hydroxy group, alkoxy group, acyl group, oxime group, amido group, propenoxy group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one X² is the abovesaid alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group; m is 0 or an integer of 1 or more; and p is an integer of 1 or more.

(4) an alkylphenoxy polysiloxane represented by the formula:



, having a number average molecular weight of less than 100,000 in which Y is the same or different substituents and each represents a member selected from the group consisting of alkyl having 1 to 3 carbon atoms, vinyl group and phenyl group; X² is a member selected from the group consisting of hydrogen atom, halogen atom, hydroxy group, alkoxy group, acyl group, oxime group, amido group, propenoxy group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one X² is the abovesaid alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group; and m is 0 or an integer of 1 or more.

(5) an alkylphenoxy polysiloxane represented by the formula:

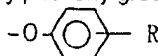


having a number average molecular weight of less than 100,000 in which Z is -R³ or -R¹-SiR²_(3-a)X²_a group; R¹ is an alkylene or aralkylene group having 2 to 20 carbon atoms which may include ether, thioether, ester or urethane bond; R² is an alkyl having 1 to 6 carbon atoms, phenyl or cycloalkyl having up to 6 carbon atoms; R³ is an alkyl having 1 to 10 carbon atoms, aryl or aralkyl group; X² is a member selected from the group consisting of hydrogen atom, halogen atom, hydroxy group, alkoxy group, acyl group, oxime group, amido group, propenoxy group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one X² is the abovementioned alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group; m is 0 or an integer of 1 or more; p is an integer of 1 or more; and a is an integer of 1 to 3.

The abovementioned silicon containing organic compounds used as an active component of the present antifouling composition are characterized in that at least one particular alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group is/are included in the molecule thereof.

The inventors, having studied silylation of various alkyl phenols, have surprisingly found that when C₇-C₁₂ alkyl substituted or 1-methyl-1-phenylethyl substituted phenoxy group(s) is (are) incorporated into silane compounds, the thus obtained organo-silicon compounds can exhibit excellent antifouling effect and higher degree of safetivity. The inventive concept was further developed to other silicon containing compounds as various silyl compounds and polysiloxanes, and on the basis of these findings, the present invention was established.

The first type of substituted phenoxy containing organo-silicon compounds used in the present invention is an organosilane containing at least one alkylphenoxy group of the formula:



in which R stands for a straight or branched chain alkyl group of the formula: C_xH_{2x+1}

in which x is an integer of 7 to 12,

or 1-methyl-1-phenylethyl group.

Such organosilanes are easily prepared by the silylation of alkyl phenols having particular alkyl groups and more specifically, by the reaction of such silyl compounds as organosilanol, organohalosilane, organoalkoxy silane and organoacyloxy silane, with an alkyl phenols through dehydration, dehydrohalogenation, dealcoholation or de-organo acidic reaction. The thus obtained alkylphenoxy group containing organo-silicon compounds are characterized in that at least one particular phenoxy silyl moiety of the formula:



in which R stands for a straight or branched chain alkyl group having 7 to 12 carbon atoms or 1-methyl-1-phenylethyl group is always included in the molecule.

The alkyl phenols to be silylated are characterized in that among 5 hydrogen atoms attached to benzene ring of the phenol, at least one hydrogen is substituted with a straight or branched chain alkyl group having 7 to 12 carbon atoms or 1-methyl-1-phenylethyl group (hereinafter called as the present alkyl phenol).

The size of alkyl group of the present alkyl phenol, i.e. carbon number, has an important meaning for the desired effects in the present invention. That is, other phenols bearing with C₁-C₆ alkyl group or cyclic hydrocarbon as phenyl or cyclohexyl group are even when silylated, not so useful in an antifouling paint because the formed silyl derivatives are easily hydrolyzed and the liberated alkyl phenols are very soluble in water. The alkyl groups having 13 or more carbon atoms are likewise undesired because such alkyl phenols, even when silylated, cannot give the desired antifouling effects. Thus, the alkyl moiety should have 7 to 12 carbon atoms or should be 1-methyl-1-phenylethyl group.

As already stated, the present alkyl phenoxy group containing organosilanes may be prepared by the reaction of silyl compounds as organosilanol, organohalosilane, organoalkoxysilane and organoacyloxysilane, with an alkyl phenols through dehydration, dehydrohalogenation, dealcoholation or de-organo acidic reaction. Examples of silyl compounds to be reacted with the present alkyl phenols are trimethyl silanol, dimethyl disilanol, triethyl silanol, triphenyl silanol, diphenyl disilanol, methylphenyl disilanol, trimethyl chlorosilane, dimethyl dichlorosilane, methyl trichlorosilane, triethyl chlorosilane, diethyl dichlorosilane, ethyl trichlorosilane, triphenyl chlorosilane, diphenyl dichlorosilane, phenyl trichlorosilane, methyl phenyl dichlorosilane, ethyl phenyl dichlorosilane, trimethylmethoxysilane, dimethyl dimethoxysilane, methyl trimethoxy silane, propyl trimethoxy silane, butyl trimethoxy silane, decyl trimethoxy silane, hexadecyl trimethoxy silane, phenyl trimethoxy silane, diphenyl dimethoxy silane, cyclohexyl methyl dimethoxy silane, gamma-aminopropyl trimethoxy silane, gamma-(2-aminoethyl)aminopropyl trimethoxy silane, gamma-(2-aminoethyl)aminopropyl methyl dimethoxy silane, vinyl trimethoxy silane, gamma-glycidoxy propylmethyl dimethoxy silane, gamma-glycidoxy propyl trimethoxy silane, gamma-methacryloxy propylmethyl dimethoxy silane, gamma-dibutylaminopropyl trimethoxy silane, gamma-methacryloxypropyl trimethoxy silane, nona-fluorobutylethyl trimethoxy silane, gamma-chloropropyl trimethoxy silane, methyl triethoxy silane, trimethyl ethoxy silane, gamma-ureidopropyl triethoxy silane, gamma-mercaptopropyl trimethoxy silane, trimethyl acetoxysilane, dimethyl diacetoxysilane, methyl triacetoxysilane, ethyl triacetoxysilane, phenyl triacetoxysilane, vinyl triacetoxysilane, n-dodecyl triethoxy silane, n-hexyl trimethoxy silane, n-octadecyl dimethyl methoxy silane, dimethyl butyl chlorosilane, dimethyloctadecyl chlorosilane and the like.

Examples of the alkylphenoxy group containing organosilanes used in the present invention are:

(In the following, alkyl represents a straight or branched C_xH_{2x+1}-group, in which x is an integer of 7 to 12, or 1-methyl-1-phenylethyl group)

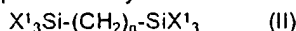
mono(alkylphenoxy) trimethyl silane

mon(alkylphenoxy) dimethyl silanol
 di(alkylphenoxy) dimethyl silane
 mon(alkylphenoxy) triethyl silane
 mono(alkylphenoxy) triphenyl silane
 5 mono(alkylphenoxy) diphenyl silanol
 di(alkylphenoxy) diphenyl silane
 mono(alkylphenoxy) methyl phenyl silanol
 di(alkylphenoxy) methyl phenyl silane
 di(alkylphenoxy) ethyl phenyl silane
 10 tri(alkylphenoxy) ethyl phenyl silane
 tri(alkylphenoxy) propyl silane
 di(alkylphenoxy) propyl methoxy silane
 mono(alkylphenoxy) dimethoxy silane
 tri(alkylphenoxy) butyl silane
 15 di(alkylphenoxy) butyl methoxy silane
 mono(alkylphenoxy) butyl dimethoxy silane
 tri(alkylphenoxy) decyl silane
 di(alkylphenoxy) decyl methoxy silane
 mono(alkylphenoxy) decyl dimethoxy silane
 20 tri(alkylphenoxy) hexadecyl silane
 di(alkylphenoxy) hexadecyl methoxy silane
 mono(alkylphenoxy) hexadecyl dimethoxy silane
 mono(alkylphenoxy) cyclohexylmethyl methoxy silane
 di(alkylphenoxy) cyclohexyl methyl silane
 25 tri(alkylphenoxy) aminopropyl silane
 di(alkylphenoxy) aminopropyl methoxy silane
 mono(alkylphenoxy) aminopropyl dimethoxy silane
 tri(alkylphenoxy) gamma-(2-aminoethyl) aminopropyl silane
 di(alkylphenoxy)-gamma-(2-aminoethyl)aminopropyl methoxy silane
 30 mono(alkylphenoxy)-gamma-(2-aminoethyl) aminopropyl dimethoxy silane
 di(alkylphenoxy) gamma-(2-aminoethyl) aminopropyl methyl silane
 mono(alkylphenoxy) gamma-(2-aminoethyl) aminopropyl methyl methoxy silane
 tri(alkylphenoxy) vinyl silane
 di(alkylphenoxy) vinyl methoxy silane
 35 mono(alkylphenoxy) vinyl dimethoxy silane
 di(alkylphenoxy) gamma-glycidoxypropyl methyl silane
 mono(alkylphenoxy) gamma-glycidoxy propylmethyl methoxy silane
 tri(alkylphenoxy) gamma-glycidoxy propyl silane
 di(alkylphenoxy) gamma-glycidoxy propyl methoxy silane
 40 mono(alkylphenoxy) gamma-glycidoxy propyl dimethoxy silane
 di(alkylphenoxy) gamma-methacryloxy propyl methyl silane
 mono(alkylphenoxy) gamma-methacryloxy propylmethyl methoxy silane
 tri(alkylphenoxy) gamma-dibutylamino propyl silane
 di(alkylphenoxy) gamma-dibutyl amino propyl methoxy silane
 45 mono(alkylphenoxy)gamma-dibutylamino propyl dimethoxy silane
 tri(alkylphenoxy) methacryloxy propyl silane
 di(alkylphenoxy) methacryloxy propyl methoxy silane
 mono(alkylphenoxy) methacryloxy propyl dimethoxy silane
 tri(alkylphenoxy) nonafluorobutyl ethyl silane
 50 di(alkylphenoxy) nonafluorobutyl ethyl methoxy silane
 mono(alkylphenoxy) nonafluorobutyl ethyl dimethoxy silane
 tri(alkylphenoxy) gamma-chloropropyl silane
 di(alkylphenoxy) gamma-chloropropyl methoxy silane
 mono(alkylphenoxy) gamma-chloropropyl dimethoxy silane
 55 tri(alkylphenoxy) gamma-ureidopropyl silane
 di(alkylphenoxy) gamma-ureidopropyl methoxy silane
 mono(alkylphenoxy) gamma-ureidopropyl dimethoxy silane
 mono(alkylphenoxy) dodecyl diethoxy silane

di(alkylphenoxy) dodecyl ethoxy silane
 mono(alkylphenoxy) hexyl dimethoxy silane
 di(alkylphenoxy) hexyl methoxy silane
 mono(alkylphenoxy) octadecyl dimethyl silane
 mono(alkylphenoxy) dimethyl butyl silane
 mono(alkylphenoxy) dimethyl octadecyl silane

and the like

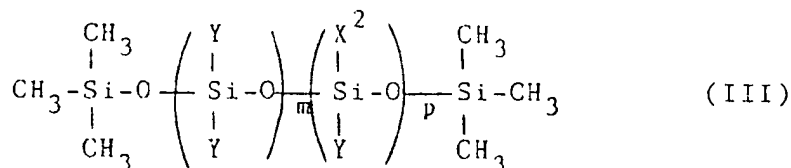
Another class of alkylphenoxy group containing organo-silicon compounds used in the present invention are alkylphenoxy bis-silyl compound represented by the formula:



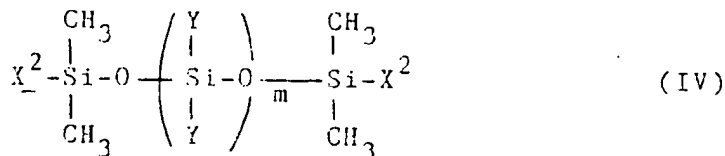
in which X^1 is selected from the group consisting of hydrogen atom, hydroxy group, lower alkyl group having 1 to 5 carbon atoms, lower alkoxy group having 1 to 5 carbon atoms, phenyl group, phenoxy group, vinyl group, acetoxy group, propenyloxy group, methyl ethyl ketoxim group, alkylphenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one of said X^1 is the straight or branched chain alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group, and n is an integer of 1 to 10.

These alkylphenoxy bis-silyl compounds may be advantageously prepared by the reaction of bis-silyl compound as alkoxy bis-silane and alkyl phenol through dealcoholic reaction.

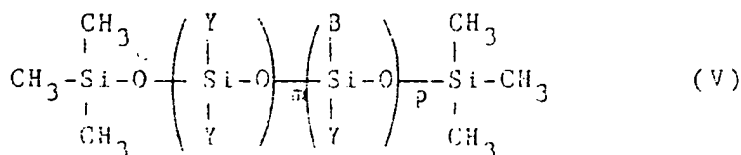
The third and fourth classes of alkylphenoxy group containing organo-silicon compounds used in the invention are the following alkylphenoxy polysiloxane represented by the formula:



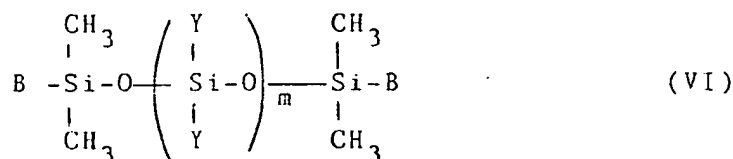
, having a number average molecular weight of less than 100,000 in which Y is the same or different substituents and each represents a member selected from the group consisting of alkyl having 1 to 3 carbon atoms, vinyl group and phenyl group; X^2 is a member selected from the group consisting of hydrogen atom, halogen atom, hydroxy group, alkoxy group, acyl group, oxime group, amido group, propenoxo group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one X^2 is the abovesaid alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group; m is 0 or an integer of 1 or more; and p is an integer of 1 or more, and the alkylphenoxy polysiloxane represented by the formula:



, having a number average molecular weight of less than 100,000 in which Y , X^2 and m are as defined above. The abovementioned alkylphenoxy polysiloxanes of the formula (III) or (IV) may be advantageously prepared by the reaction of polysiloxane compounds represented by the formula:



or



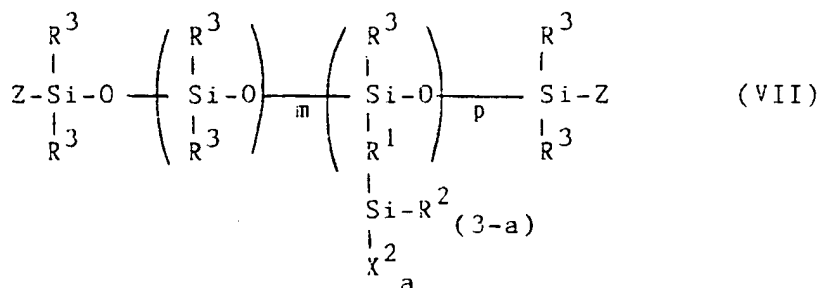
in which Y is the same or different substituents and each represents a member selected from the group consisting of alkyl having 1 to 3 carbon atoms, vinyl group and phenyl group, m is 0 or an integer of 1 or more, p is an integer of 1 or more and B is hydrogen atom, halogen atom, hydroxy group or acyl group, and an alkyl phenol whose alkyl group is a straight or branched chain alkyl having 7 to 12 carbon atoms or 1-methyl-1-phenylethyl phenol or reactive derivatives thereof, in the presence of an appropriate catalyst as organoperacid, fatty acid azo compound, organometallic compound and the like, under heating or illuminating with UV rays, while removing the produced water, alcohol, organic acid, hydrogen halide, oxime, amine or amide out of the system, thereby introducing the alkylphenoxy group or 1-methyl-1-phenylethyl phenoxy group in all or part of B positions.

Alternatively, the alkylphenoxy polysiloxane represented by the formula (III) or (IV) may be prepared by polymerizing a polymerizable silane compound as hydroxy silane, halogenized silane or the like previously introduced with the abovementioned alkylphenoxy or 1-methyl-1-phenylethyl group and other polymerizable silane compound through dehydration, hydrolysis or condensation reaction.

Examples of the the alkylphenoxy polysiloxane of the formula (III) are methyl alkylphenoxy silicone oil obtained by the reaction of methyl hydrogen silicone oil (B=hydrogen atom) and alkyl phenol; methyl alkylphenoxy silyl alkyl silicone oil obtained by the reaction of alkoxy silyl alkyl silicone oil (B=methyl) and alkyl phenol and the like.

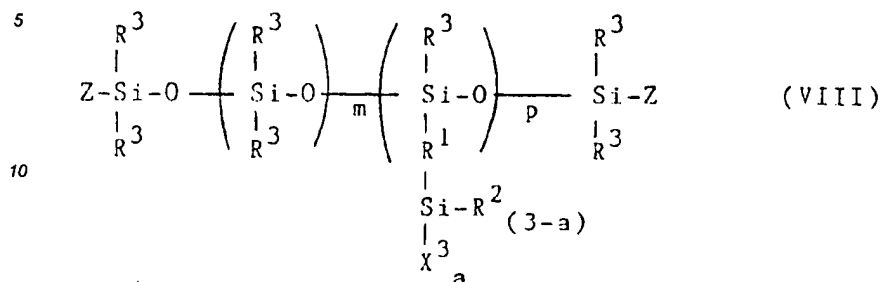
Examples of the alkylphenoxy polysiloxane of the formula (IV) are endo alkyl-phenoxy dimethyl polysiloxane obtained by the reaction of endo-silanol containing dimethyl polysiloxane (B=HO) and alkyl phenol; endo alkyl-phenoxy methylphenyl polysiloxane obtained by the reaction of endo silanol containing methyl phenyl polysiloxane and alkyl phenol; endo alkyl-phenoxy methyl phenyl polysiloxane obtained by the reaction of endo alkoxy silyl containing methyl phenyl polysiloxane (B= alkoxy having 1 to 4 carbon atoms) and alkyl phenol; endo alkyl-phenoxy dimethyl diphenyl polysiloxane obtained by the reaction of endo alkoxy silyl containing dimethyl diphenyl polysiloxane (B= alkoxy having 1 to 4 carbon atoms) and alkyl phenol; endo alkyl-phenoxy methyl propyl polysiloxane obtained by the reaction of endo silanol containing methyl propyl polysiloxane (B=HO) and alkyl phenol; and endo alkyl-phenoxy dimethyl polysiloxane obtained by the reaction of dimethyl hydrogen polysiloxane (B=H) and alkyl phenol.

The fifth class of alkylphenoxy group containing organo-silicon compounds used in the present invention is an alkylphenoxy polysiloxane represented by the formula:



having a number average molecular weight of less than 100,000, in which Z is $-\text{R}^3$ or $-\text{R}^1 - \text{SiR}^2_{(3-a)}\text{X}^2_a$ group; R^1 is an alkylene or aralkylene group having 2 to 20 carbon atoms which may include ether, thioether, ester or urethane bond; R^2 is an alkyl having 1 to 6 carbon atoms, phenyl or cycloalkyl having up to 6 carbon atoms; R^3 is an alkyl having 1 to 10 carbon atoms, aryl or aralkyl group; X^2 is a member selected from the group consisting of hydrogen atom, halogen atom, hydroxy group, alkoxy group, acyl group, oxime group, amido group, propenoxy group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms and 1-methyl-1-phenylethyl phenoxy group, providing that at least one X^2 is the abovesaid alkyl phenoxy group or 1-methyl-1-phenylethyl phenoxy group; m is 0 or an integer of 1 or more; p is an integer of 1 or more; and a is an integer of 1 to 3.

Such alkylphenoxy polysiloxanes (VII) may be advantageously prepared by the reaction of organopolysiloxanes (VIII) reported in Japanese Patent Publication(unexamined) No 43454/92 and represented by the formula:



in which Z, R¹, R², R³ m, p, a are as defined above, and X³ is an alkoxy group having 1 to 4 carbon atoms, and at least one phenol having C₇ - C₁₂ straight or branched alkyl group or 1-methyl-1-phenylethyl group.

The present antifouling paint consists essentially of the above mentioned alkyl phenoxy group containing organo-silicon compound and a solvent, the amount of said organo-silicon compound being 5 to 100% by weight of the total solid of the paint. The solvent used may be water, an organic solvent or mixture thereof.

The present paint may further contain a resin which is common in a coating composition.

For example, in a solvent type paint, the following may be used each singularly or in the combination of two or more, as desired: vinyl chloride resin, chlorinated rubber, chlorinated polyethylene, chlorinated polypropylene, acrylic resin, styrenebutadiene polymer, polyester resin, epoxy resin, polyamide resin, petroleum resin, silicone resin, silicone rubber, wax, paraffin, rosin ester, rosin resin, and a resin having in its side chains such metal as tin, copper, zinc, tellurium and the like.

Examples of the resins used in an aqueous paint, are acryl emulsion resin, epoxy emulsion resin, vinyl acetate resin and the like.

If required, the present paint may be added with other known antifouling agent as co-toxicant, plasticizer, colorant, body pigment, solvent and the like. In preparing the present antifouling paint, any of the conventional preparation techniques may be satisfactorily used.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and % are by weight.

Manufacturing Example 1

Into a reaction vessel fitted with a decanter, were placed 262 parts of n-decyl trimethoxy silane, 220 parts of nonyl phenol and 2.4 parts of tetra-n-butoxy titanium and the mixture was heated to 120°C in 30 minutes. Thereafter, the condensation reaction was effected at 120°-200°C for 5 hours, during which time 31 parts of methanol were recovered. Thus obtained alkyl phenoxy containing silane compound A was a slightly brown-colored clear liquid having a viscosity of 3.5 poise.

Manufacturing Example 2

Into a reaction vessel, were placed 19.1 parts of phenylmethyl dichlorosilane, 252 parts of toluene and 8.7 parts of puridine and the mixture was heated to 40°C. To this, 44 parts of nonyl phenol were dropwise added in one hour and the combined was maintained at the same temperature for 5 hours. Thus obtained white turbid liquid was filtered and from the filtrate, toluene was removed off by using an evaporater. Thus obtained alkyl-phenoxy containing silane compound B was a clear liquid, whose viscosity was 12 poise.

Manufacturing Example 3

Into a reaction vessel fitted with a fractionating column, were placed 120 parts of dimethyl dimethoxy silane, 440 parts of nonyl phenol and 3.0 parts of tetra-n-butoxy titanium and the mixture was heated to 75°C in 20 minutes. Thereafter, the condensation reaction was effected at 75° to 80°C for 3 hours, during which time 60 parts of methanol were recovered. Thus obtained nonyl phenoxy dimethyl silane C was a colourless clear liquid having a viscosity of 0.1 poise.

Manufacturing Example 4

Into a reaction vessel fitted with a fractionating column, were placed 130 parts of phenyl trimethoxy silane, 425 parts of 4-(1-methyl-1-phenylethyl) phenol and 3.0 parts of tetra-n-butoxy titanium and the mixture was heated to 100°C in 30 minutes. Thereafter, the condensation reaction was effected at temperature of up to 200°C for 3 hours, during which time 53 parts of methanol were recovered. Thus obtained substituted phenoxy containing silane D was a pale brown clear liquid having a viscosity of 21 poise.

Examples 1 - 7

Various paints were prepared by mixing the indicated amounts of components in Table 1 by using a high speed homodisper.

Thus obtained paints each was applied on sand papered hard vinyl chloride plate (30 x 10 x 0.3 cm) in about 100 microns dry thickness.

Comparative Examples 1 - 2

Using the materials shown in Table 2 and following the procedures of Examples 1 - 6, comparative paints were prepared and applied on the similar vinyl chloride plate.

In Table 2, amylphenoxy dimethyl silane was prepared by using the same procedures as stated in Manufacturing Example 3 but substituting p-t-amyl phenol for nonyl phenol.

Table 1

Example	1	2	3	4	5	6	7
compound A	25				10		
compound B		25				10	
Compound C			25	5	10	10	
Compound D							25
KE-45-TS(*1)	50	50	50	50	50	50	50
KF-96 (*2)	10	10	10	20	15	15	15
petrolatam(*3)	5	5	5	20	15	15	15
xylene	10	10	10	5	-	-	10
Total	100	100	100	100	100	100	100

*1..1 liquid type RTV silicone rubber (NV=50%) (Shinetsu Chem.Co.)

*2..dimethyl silicone oil (NV=100%) (Shinetsu Chem. Co.)

*3.. JIS K-2235 Petrolatam No. 4

Table 2

Comp. Example	1	2		
compound A				
compound B				
Compound C				
amyl phenoxy dimethyl silane	25			
KE-45-TS(*1)	50	50		
KF-96 (*2)	10	20		
petrolatam(*3)	5	20		
xylene	10	10	-	-
Total	100	100		

The coated plates obtained in Examples 1 - 7 and Comparative Examples 1 - 2 and uncoated plate were placed in sea water in 1 meter depth at Tamano City, Okayama Pref. and antifouling effects were evaluated. The test results are shown in Table 3.

Table 3

Test duration (month)	1	2	3	4	6
Example 1	0	0	0	0	0
Example 2	0	0	0	0	0
Example 3	0	0	0	0	0
Example 4	0	0	0	0	0
Example 5	0	0	0	0	0
Example 6	0	0	0	0	0
Example 7	0	0	0	0	0
Comp. Ex.1	0	0	5	10	20
Comp. Ex.2	0	5	10	30	50
Uncoated	10	30	50	60	30

(each figure shows stained area %)

Manufacturing Example 5

Into a reaction vessel fitted with a fractionating column, were placed 326 parts of 1,6-bis(trimethoxysilyl) hexane, 440 parts of nonyl phenol and 3.0 parts of tetra-n-butoxy titanium and the mixture was heated under normal pressure to 120°C in 30 minutes. Thereafter, the condensation reaction was effected at 120°-180°C for 4 hours, during which time 60 parts of methanol were recovered. The reaction was confirmed by the infra red absorption spectrum, i.e. appearance of absorption peak at 940 cm⁻¹ caused by phenoxysilyl and disappearance of absorption peak at 3400 cm⁻¹ caused by the hydroxyl group of nonyl phenol. Thus obtained alkyl phenoxy bissilyl compound E was a clear liquid having a viscosity of 2.0 poise.

Manufacturing Example 6

Into a reaction vessel fitted with a fractionating column, were placed 326 parts of 1,6-bis(trimethoxysilyl) hexane, 576 parts of heptyl phenol and 3.0 parts of tetra-n-butoxy titanium and the mixture was heated under normal pressure to 120°C in 30 minutes. Thereafter, the condensation reaction was effected at 120°-150°C for 4 hours, during which time 90 parts of methanol were recovered. The reaction was confirmed by the infra red absorption spectrum, i.e. appearance of absorption peak at 940 cm⁻¹ caused by phenoxysilyl and disappearance of absorption peak at 3400 cm⁻¹ caused by the hydroxyl group of heptyl phenol. Thus obtained alkyl phenoxy bissilyl compound F was a clear liquid having a viscosity of 18.0 poise.

Manufacturing Example 7

Into a reaction vessel fitted with a fractionating column, were placed 326 parts of 1,6-bis(trimethoxysilyl) hexane, 1320 parts of nonyl phenol and 5.0 parts of tetra-n-butoxy titanium and the mixture was heated under normal pressure to 120°C in 30 minutes. Thereafter, the condensation reaction was effected at 120°-200°C for 5 hours, during which time 180 parts of methanol were recovered. The reaction was confirmed by the infra red absorption spectrum, i.e. appearance of absorption peak at 940 cm⁻¹ caused by phenoxysilyl and disappearance of absorption peak at 3400 cm⁻¹ caused by the hydroxyl group of nonyl phenol. Thus obtained alkyl phenoxy bissilyl compound G was a clear liquid having a viscosity of 64.0 poise.

Manufacturing Example 8

Into a reaction vessel fitted with a fractionating column, were placed 326 parts of 1,6-bis(trimethoxysilyl) hexane, 1048 parts of dodecyl phenol and 5.0 parts of tetra-n-butoxy titanium and the mixture was heated under normal pressure to 120°C in 30 minutes. Thereafter, the condensation reaction was effected at 120°-200°C for 5 hours, during which time 125 parts of methanol were recovered. The reaction was confirmed by the infra red absorption spectrum, i.e. appearance of absorption peak at 940 cm⁻¹ caused by phenoxysilyl and disappearance of absorption peak at 3400 cm⁻¹ caused by the hydroxyl group of dodecyl phenol. Thus obtained alkyl phenoxy bissilyl compound H was a clear liquid having a viscosity of 50.0 poise.

Manufacturing Example 9

Into a reaction vessel fitted with a fractionating column, were placed 110 parts of 1,6-bis(trimethoxysilyl) hexane, 425 parts of 4-(1-methyl-1-phenylethyl) phenol and 2.5 parts of tetra-n-butoxy titanium and the mixture was heated under normal pressure to 100°C in 30 minutes. Thereafter, the condensation reaction was effected at temperature of up to 200°C for 3 hours, during which time 54 parts of methanol were recovered. The reaction was confirmed by the infra red absorption spectrum, i.e. appearance of absorption peak at 940 cm⁻¹ caused by phenoxysilyl and disappearance of absorption peak at 3400 cm⁻¹ caused by the hydroxyl group of 4-(1-methyl-1-phenylethyl) phenol. Thus obtained substituted phenoxy bissilyl compound I was a clear liquid having a viscosity of 45.0 poise.

Examples 8-16 and Comparative Examples 3-4

The alkyl phenoxy bissilyl compounds and other materials shown in Table 4 were mixed and dispersed well by means of SG mill with glass beads and the antifouling paints were prepared. Next, the present antifouling paints and comparative paints each was applied on a commercialized test steel plate previously coated with a conventional antifouling paint (100 x 300 mm) in a dry film thickness of 60 to 80 microns and dried for 1 day. Thus prepared test plates were dipped in sea water in 1 m depth at Tamano City, Okayama Pref. and degree of stain was examined. As a control, the commercialized test plate was tested in Comparative Example 4. The test results are shown in Table 5.

Table 4

paint composition										
	Example									Comp. Ex.
	8	9	10	11	12	13	14	15	16	3
Compound E	20				10		10			
Compound F		20								
Compound G			20			5		10		
Compound H				20	10					
Compound I									20	
Raloflex MP-45	25	25	25	25	25	25			25	25
WW rosin	25	25	25	25	25	25			25	25
cuprous oxide						15				30
fluid paraffin								5		
KE45-TS							60	50		
SH-510 oil								5		
dioctyl phthalate	1	1	1	1	1	1			1	1
colloidal silica	1	1	1	1	1	1			1	1
xylene	20	20	20	20	20	20	30	30	20	15
MBK	8	8	8	8	8	8			8	3
total			100							100

Raloflex MP-45..vinyl chloride.vinylisopropyl ether copolymer manufactured by BASF
 fluid paraffin..JIS K2231
 KE45 .. I liquid type room temp. curing silicone rubber
 SH-510 oil .. methyl phenyl silicone oil, manufactured by Toray Silicone

Table 5

Sea water immersion test(stained area %)					
time duration	1	3	6	12	24 months
Example 8	0	0	0	0	5
Example 9	0	0	0	0	5
Example 10	0	0	0	0	5
Example 11	0	0	0	0	5
Example 12	0	0	0	0	3
Example 13	0	0	0	0	5
Example 14	0	0	0	0	3
Example 15	0	0	0	0	3
Example 16	0	0	0	0	5
Comp.Ex. 3	0	0	10	30	50
Comp.Ex. 4	10	30	50	70	100

Manufacturing Example 10

Into a reaction vessel fitted with a decanter, were placed 100 parts of both ends alkoxy silyl methylphenyl polysiloxane (OCH₃ 15wt%, viscosity 9.9 poise), 107 parts of nonyl phenol and 1.0 parts of tetra-*i*-propoxy titanium and the mixture was heated under normal pressure to 120°C in 30 minutes, to 220°C in 1.5 hours and then to 240°C in 4.5 hours to effect condensation reaction, during which time 12.4 parts of methanol were recovered. Thus obtained alkyl phenoxy silyl containing polysiloxane J was a slightly brown clear viscous liquid having a viscosity of 71 poise.

Manufacturing Example 11

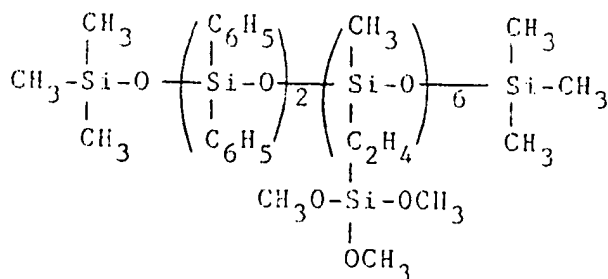
Into a reaction vessel, were placed 20 parts of both ends SiH dimethyl hydrogen polysiloxane (MW= 1,000; viscosity 0.07 poise), 8.8 parts of nonyl phenol and 0.01 part of 2wt% chloroplatinic acid-isopropanol solution and the combined was heated to 100°C and effected dehydration reaction for 5 hours. Thus obtained alkyl-phenoxy silyl containing polysiloxane K was a clear liquid having a viscosity of 8.5 poise.

Manufacturing Example 12

Into a reaction vessel, were placed 20 parts of methyl hydrogen silicone oil having hydrogen atom at the main chain Si (MW= 1,000; viscosity 0.3 poise), 50 parts of nonyl phenol and 0.03 part of 2wt% chloroplatinic acid-isopropanol solution and the combined was heated to 100°C and effected dehydration reaction for 5 hours. Thus obtained methylalkylphenoxy silicone oil L was a clear liquid having a viscosity of 9.0 poise.

Manufacturing Example 13

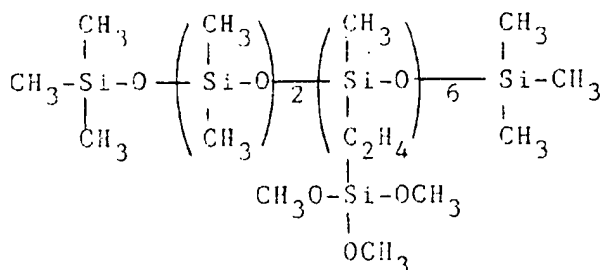
Into a reaction vessel fitted with a decanter, were placed 158 parts of alkoxy silylalkyl group containing organopolysiloxane represented by the formula:



220 parts of nonyl phenol and 2.0 parts of tetra-*i*-propoxy titanium and the mixture was heated under normal pressure to 120°C in 30 minutes, to 180°C in 2 hours and then to 220°C in 2 hours to effect condensation reaction, during which time 29.0 parts of methanol were recovered. Thus obtained alkyl phenoxy silyl containing polysiloxane M was a pale brown clear viscous liquid having a viscosity of 70 poise.

Manufacturing Example 14

Into a reaction vessel, were placed 92 parts of alkoxy silyl alkyl group containing organo- polysiloxane represented by the formula:



212 parts of 4-(1-methyl-1-phenylethyl) phenol and 1.5 parts of tetra-*i*-propoxy titanium and the combined was heated to 120°C in 1 hour, to 190°C in 1 hour and then to 220°C in 2.5 hours to effect condensation reaction. During which time, 28.8 parts of methanol were recovered. Thus obtained substituted phenoxy silyl containing polysiloxane N was a pale brown clear viscous liquid having a viscosity of 85 poise.

Examples 17 - 24

The materials shown in Table 6 were mixed well by using a high speed homodisper to obtain the present antifouling paints. Each paint was applied onto a sand papered hard vinyl chloride plate (30 x 10 x 0.3 cm) in a dry film thickness of about 100 microns.

Comparative Examples 5 and 6

Using the materials shown in Table 7, the similar paints were prepared as in Examples 17-24.

The thus obtained coated plates were dipped in sea water in 1 m depth at Tamano City, Okayama Pref. and evaluated the stain degree. The test results are shown in Table 8.

Table 6

Example	17	18	19	20	21	22	23	24
compound J	25				10			
compound K		25				10		
Compound L			25	5	10	10		
Compound M							25	
Compound N								25
amylphenoxy methyl								
phenyl polysiloxane								
vinyl chloride resin								
KE-45-TS	50	50	50	50	50	50	50	50
KF-96	10	10	10	20	15	15	10	10
fluid paraffin	5	5	5	20	15	15	5	5
petrolatam								
xylene	10	10	10	5			10	10
Total	100	100	100	100	100	100	100	100

Table 7

Comp. Example	5	6
amylphenoxy methyl		25
phenyl polysiloxane		
vinyl chloride resin		
KE-45-TS	50	50
KF-96	20	10
fluid paraffin	20	5
petrolatam		
xylene	10	10
Total	100	100

Table 8

Antifouling test (stain area %)							
dipping time (month)	1	3	6	9	12	18	24
Example 17	0	0	0	0	0	0	5
Example 18	0	0	0	0	0	0	5
Example 19	0	0	0	0	0	0	5
Example 20	0	0	0	0	0	0	10
Example 21	0	0	0	0	0	0	5
Example 22	0	0	0	0	0	0	5
Example 23	0	0	0	0	0	0	5
Example 24	0	0	0	0	0	0	5
Comp.Ex. 5	5	25	40	50	80	100	100
Comp.Ex. 6	0	10	10	10	50	80	100
Uncoated	10	50	80	100	100	100	100

Examples 25-30

Antifouling treating agents for fishnet use were prepared by mixing the materials shown in Table 9 by a high speed homodisper. Polyethylene fishnets (100 x 100 cm) were dipped into the thus prepared compositions and dried.

Comparative Examples 7 and 8

The similar experiments were carried out using the materials shown in Table 10 for the treating compositions.

Thus obtained fishnets were immersed in sea water in 1 m depth at Tamano City, Okayama Pref. and evaluated the antifouling effects. The test results are shown in Table 11.

Table 9

Example	25	26	27	28	29	30
compound J	30					
compound K		20		5		
Compound L			20			
Compound M						
Compound N					20	5
amylphenyl methyl						
phenyl polysiloxane						
vinyl chloride resin				10		10
KE-45-TS						
KF-96						
fluid paraffin	5	5	5	5	5	5
petrolatam	5	5	5	5	5	5
xylene	60	70	70	75	70	75
Total	100	100	100	100	100	100

Table 10

Comp. Example	7	8
compound H		
compound I		
Compound J		
amylphenoxy methyl		30
phenyl polysiloxane		
vinyl chloride resin	15	
KE-45-TS		
KF-96		
fluid paraffin	5	5
petrolatam	5	5
xylene	75	60
Total	100	100

Table 11

Antifouling test (clogging area %)					
dipping time (month)	1	2	3	5	6
Example 25	0	0	0	0	0
Example 26	0	0	0	0	5
Example 27	0	0	0	0	5
Example 28	0	0	0	0	5
Example 29	0	0	0	0	0
Example 30	0	0	0	0	0
Comp.Ex. 7	20	40	80	100	100
Comp.Ex. 8	0	10	30	50	80
Uncoated	30	50	90	100	100

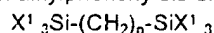
Claims

1. An antifouling paint comprising an alkylphenoxy group-containing organo-silicon compound and a solvent, the alkyl substituent being a straight or branched C_7 to C_{12} alkyl group or a 1-methyl-1-phenylethyl group.
2. An antifouling paint according to claim 1 in which the alkyl phenoxy group-containing organo-silicon compound forms from 5 to 100% by weight of the non-volatile content of the paint.
3. An antifouling paint according to claim 1 or claim 2 in which the alkyl phenoxy group-containing organo-silicon compound is an organo-silane having in its molecule at least one alkylphenoxy group represented by the formula:



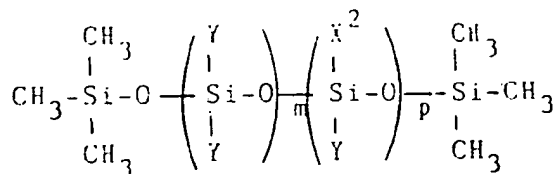
in which R is a straight or branched chain alkyl group of the formula: C_xH_{2x+1} (in which x is 7 to 12) or a 1-methyl-1-phenylethyl group.

4. An antifouling paint according to any one of the preceding claims in which the alkyl phenoxy group-containing organo-silicon compound is an alkylphenoxy bis-silyl compound of the formula:



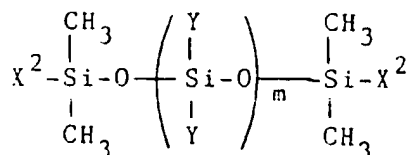
in which each group X^1 is a hydrogen atom, hydroxy group, lower alkyl group having 1 to 5 carbon atoms, lower alkoxy group having 1 to 5 carbon atoms, phenyl group, phenoxy group, vinyl group, acetoxy group, propenyloxy group, methyl ethyl ketoxim group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms or a 1-methyl-1-phenylethyl phenoxy group, provided that at least one group X^1 is a straight or branched chain alkyl having 7 to 12 carbon atoms or a 1-methyl-1-phenylethyl phenoxy group; and n is an integer of from 1 to 10.

5. An antifouling paint according to any one of claims 1-3 in which the alkyl phenoxy group-containing organo-silicon compound is an alkylphenoxy polysiloxane having a number average molecular weight of less than 100,000 and having the formula:



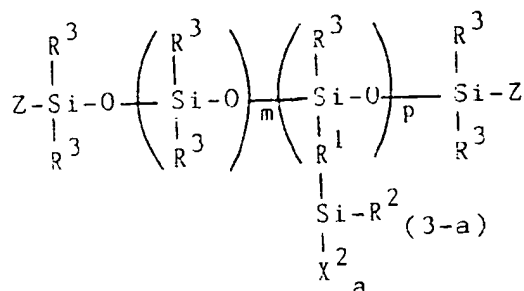
in which the group Y are the same or different and each is an alkyl group having 1 to 3 carbon atoms, a vinyl group or a phenyl group; X² is a hydrogen atom, halogen atom, hydroxy group, alkoxy group, acyl group, oxime group, amido group, propenoxy group, alkyl phenoxy group whose alkyl is a straight or branched chain alkyl having 7 to 12 carbon atoms, or a 1-methyl-1-phenylethyl phenoxy group, provided that at least one X² is the said alkylphenoxy group or 1-methyl-1-phenylethylphenoxy group; m is 0 or an integer of 1 or more; and p is an integer of 1 or more.

6. An antifouling paint according to any one of claims 1-3, wherein the alkyl phenoxy group-containing organo-silicon compound is an alkylphenoxy polysiloxane, having a number average molecular weight of less than 100,000 and having the formula:



in which Y, X², and m have the meanings as defined in claim 5.

7. An antifouling paint according to any one of claims 1-3 in which the alkyl phenoxy group-containing organo-silicon compound is an alkylphenoxy polysiloxane, having a number average molecular weight of less than 100,000 and having the formula:



in which Z is a -R³ or -R¹-SiR²_(3-a)X²_a

group; R¹ is an alkylene or aralkylene group having 2 to 20 carbon atoms which may include ether, thioether, ester or urethane bond; R² is an alkyl having 1 to 6 carbon atoms, phenyl or cycloalkyl having up to 6 carbon atoms; R³ is an alkyl having 1 to 10 carbon atoms, aryl or aralkyl group; X² has the meaning defined in claim 5; m is 0 or an integer of 1 or more; p is an integer of 1 or more; and a is an integer of 1 to 3.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 2535

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	DE-A-3 830 427 (KANSAI PAINT) * claims 11-14; example 3 *	1-4	C09D5/14 C09D183/04
D,A	EP-A-0 408 352 (NIPPON PAINT) * claims 1-3 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08 JUNE 1993	Examiner KLIER E.K.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background U : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons @ : member of the same patent family, corresponding document</p>			

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